



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## ENERGY & ENVIRONMENT DIVISION

Presented at the American Chemical Society Symposium on  
"Nuclear and Chemical Dating Techniques", Houston, Texas  
March 23-28, 1980

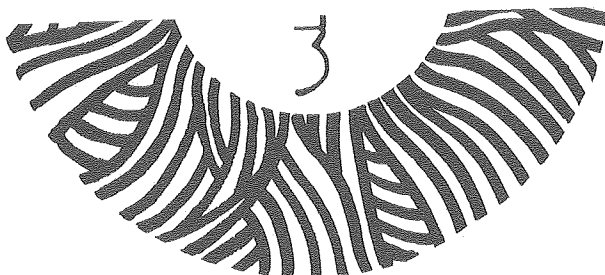
RESULTS OF A DATING ATTEMPT - CHEMICAL AND PHYSICAL MEASUREMENTS  
RELEVANT TO THE CAUSE OF THE CRETACEOUS TERTIARY EXTINCTIONS

Frank Asaro, Helen V. Michel, Luis W. Alvarez, and  
Walter Alvarez

September 1980

### TWO-WEEK LOAN COPY

*This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 6782.*



## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

RESULTS OF A DATING ATTEMPT - CHEMICAL AND PHYSICAL  
MEASUREMENTS RELEVANT TO THE CAUSE OF THE CRETACEOUS  
TERTIARY EXTINCTIONS\*\*\*

Frank Asaro\*, Helen V. Michel,\* Luis W. Alvarez,<sup>†</sup>\*  
and Walter Alvarez\*\*

In Gubbio, Italy, a 1 cm layer of clay between extensive limestone formations marks the boundary between the Cretaceous and Tertiary Periods. This clay layer was known to have been deposited about 65 million years ago when many life forms became extinct, but the length of time associated with the deposition was not known. In an attempt to measure this time with normally deposited meteoritic material as a clock, extensive measurements of iridium abundances (and those of many other elements) were made on the Gubbio rocks. Neutron activation analysis was the principal tool used in these studies. About 50 elements are searched for in materials like the earth's crust, about 40 are detected and about 30 are measured with useful precision. (26-28)

We were not able to determine exactly how long the clay deposition took. Instead the laboratory studies on the chemical and physical nature of the Cretaceous-Tertiary boundary led to the theory that an asteroid collision with the earth was responsible for the extinction of many forms of life including the dinosaurs.

---

\* Lawrence Berkeley Laboratory.

\*\* University of California at Berkeley, Department of Geology and Geophysics.

\*\*\* Incorporated in this paper are data and references that were acquired after the Symposium and before September 1, 1980.

<sup>†</sup> University of California, Space Sciences Laboratory.

### Experimental Research

Our research to date has demonstrated that deep-sea limestones exposed in Italy,<sup>(1-3)</sup> Denmark,<sup>(1)</sup> New Zealand<sup>(4)</sup> and northern Spain<sup>(6)</sup> show unusual increases in the abundance of iridium (Ir) above the background level at exactly the time of the Cretaceous-Tertiary (C-T) extinctions, 65 million years ago. As Ir is much depleted on the earth's surface with respect to the average solar system abundance, such an enrichment is not likely to have come from a terrestrial source. Extraterrestrial sources, however, contain 3 orders of magnitude more Ir than terrestrial sources and are much more likely to have produced the enrichment. Measurement of the isotopic ratio of the two iridium isotopes in the Italian C-T boundary layer showed that it was identical with that of a terrestrial source<sup>(1)</sup>, and hence the iridium originated from within the solar system. The solar system origin of the iridium rules out an interstellar origin for the asteroid as postulated by Napier and Clube for impacting planetesimals.<sup>(29)</sup> Many sources of extraterrestrial material from within the solar system were considered<sup>(1)</sup> and subjected to three tests. They had to be (1) able to deposit the Ir, (2) able to cause the C-T extinctions and (3) likely to occur in a period of ~65 million years. Only one source survived the tests.

### Asteroid-Impact Hypothesis

We have developed an asteroid-impact theory that satisfied these conditions and many others<sup>(1)</sup>. The theory assumes the following events. An Apollo object, with about a 10 km diameter struck the earth 65 million years ago. It vaporized as did a much larger mass of terrestrial

material. About 20 percent of this combined mass (modeled after the volcanic explosion of Krakatoa) ended up in the stratosphere, encircled the earth and blocked out nearly all of the direct sunlight. Photosynthesis then stopped. The larger animals which depended on the plant food chain died while some of the smaller ones (needing less food) survived. Some seeds could have survived for several years and then re-established the plants after the dust cloud sank to the earth and the direct sunlight reappeared. Mass extinctions of this type have occurred about every 100 million years.

#### Checking of Hypothesis

Four different ways of calculating the asteroid diameter all give a value of ~10 km and this consistency lends confidence to the asteroid-impact theory. The Ir anomaly was first observed by us in Italian rock. Our theory predicted that the unusually abundant Ir should appear all over the world where the C-T boundary is exposed (intact). Part of the hypothesis was confirmed when the anomalously high Ir abundance was found in the C-T boundary layers in Denmark, northern and south-east Spain and half-way round the world in New Zealand. Another prediction of the theory is that a component of the clay layer at the C-T boundary would be different in composition from other clays in the same section because it contained a component from the impact site. This prediction was confirmed in measurements of the Italian and Danish sections<sup>(1)</sup>.

#### Other Work

Dutch geologists, after learning of the Italian Ir data, found a similar Ir anomaly in a rock section from Caravaca (Barranco-del-Gredero)

in south-east Spain.<sup>(5)</sup> On a sample kindly supplied by J. Smit from this section we were able to confirm the iridium abundances and determine the variation in abundance within a few centimeters of the C-T boundary.<sup>(7)</sup> Smit and Hertogen<sup>(5)</sup> also measured the abundances of another platinum group element, osmium, and it also exhibited an anomalously high abundance at the C-T boundary near Caravaca. These authors also stated the ratio of two osmium isotopes in the C-T boundary was indistinguishable within 0.1 percent from the terrestrial (i.e., solar system) ratio.

A concern has been expressed<sup>(8,9)</sup> about the correctness of the stratigraphy upon which the selection<sup>(1)</sup> of our Italian samples was based. Very recent work<sup>(10)</sup> on a deep-sea core from the southeastern Atlantic Ocean near South Africa, however, supported the Italian stratigraphy.

There have been a number of suggestions in the past that an extra-terrestrial object impacting on the earth caused or could cause massive extinctions of life. E. J. Öpik,<sup>(11)</sup> for example, discussed the lethal effects which could be caused by the heat generated from such objects striking the earth, and H. C. Urey<sup>(12)</sup> stated specifically that a comet was probably the cause of the Cretaceous-Tertiary extinctions. There have also been science fiction stories and a movie relating to the effects. The things likely to occur if the sunlight were temporarily "turned off" have also been discussed.<sup>(13)</sup> Our deduction in contrast to the others is based on physical science data (the iridium anomaly) and is the only explanation we found which explained the Ir anomaly, could cause the massive extinction of life and was likely to occur in a period of ~100 million years.

Smit and Hertogen<sup>(5)</sup> also concluded a large meteorite may have struck the earth and caused the extinctions. K. J. Hsu<sup>(14)</sup> suggested the extinctions were caused by cyanide poisoning resulting from a cometary impact, and Cesare Emiliani<sup>(15)</sup> had the suggestion that a sudden heat flash, possibly caused by an asteroid impact, could have caused the C-T extinctions. Ganapathy<sup>(19)</sup> measured the abundances of Pt group elements (Ru, Pd, Re, Os, Ir, Pt), Au, Co and Ni in the Danish C-T boundary layer and confirmed that it contained a chondritic components.

#### Future Directions

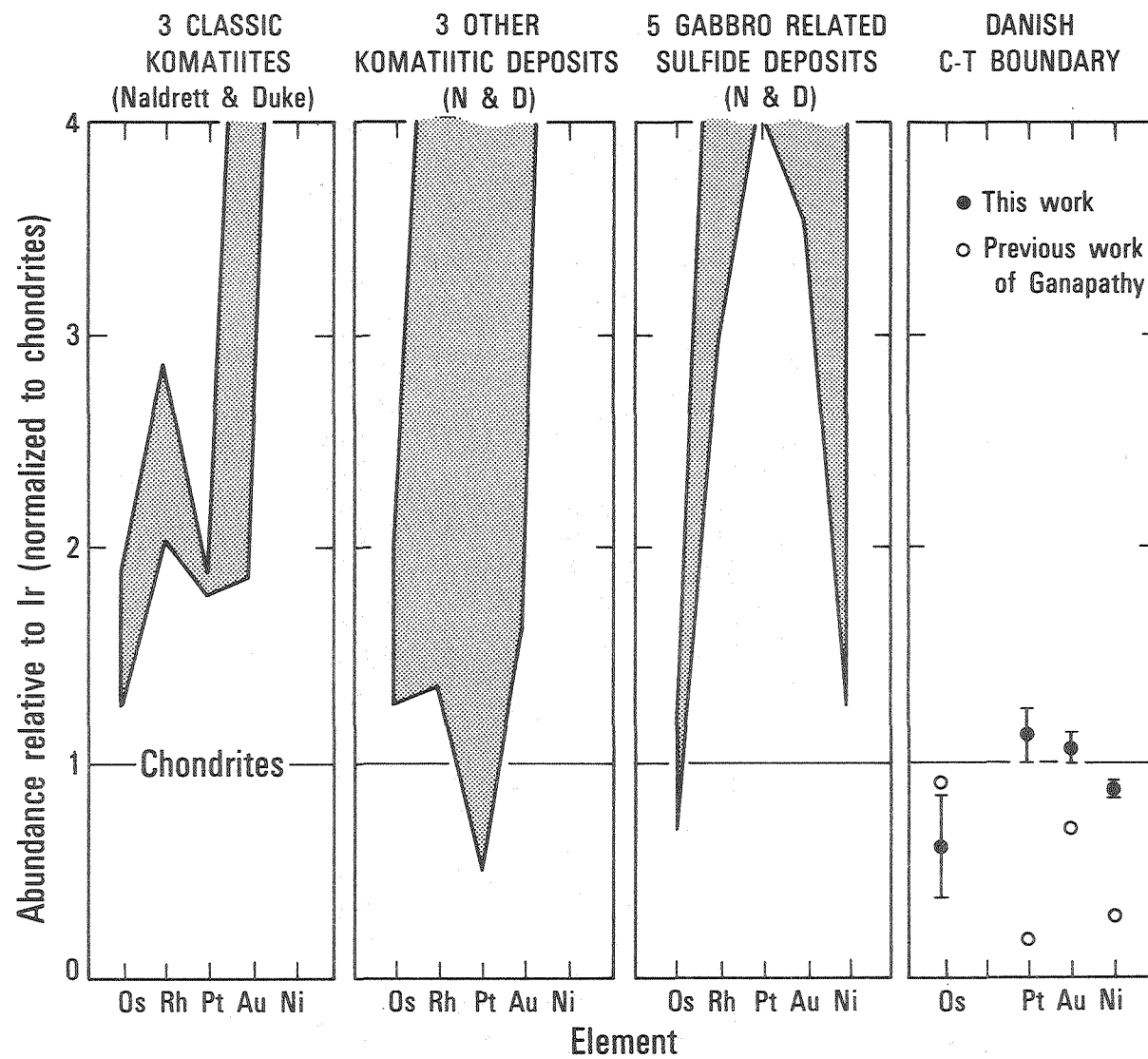
The Ir anomaly has been observed in uplifted marine sediments in five locations in Italy, one in Denmark, two in Spain and one in New Zealand. It has not been found yet in continental sediments or deep-sea cores. If the asteroid-impact theory is valid, the Ir anomaly should be found wherever the C-T boundary is intact.

Additional measurements of the abundances of platinum group elements should be made in C-T boundary layer samples. Figure 1 shows the ratio of abundances of different elements to that of Ir in various mantle materials, divided by the same quantities for C1 chondrites.<sup>(16)</sup> The Pt and Au ratios approach the chondritic abundances as the degree of partial melting of the mantle gets higher. An ultra-basic nodule,<sup>(17)</sup> which may represent the mantle, has very close to the chondritic ratios for Ir and Pt. Some of our recent measurements of Pt, Au and non-volatile Os as well as Ir in the Danish C-T boundary layer are shown in Fig. 1 and Table I. The Pt and Ir data are consistent with a chondritic origin as predicted by the asteroid-impact theory. Part of

## Figure 1.

Relative abundances of some platinum group elements, gold and nickel with respect to iridium. Each abundance was divided by the abundance of that element (except for Rh) in Type I carbonaceous chondrites. Rh abundances were divided by Rh abundances in other types of chondrites as CI values were not available. Errors in the LBL measurements reflect one sigma value of the counting errors except for the Au error. The latter is the root mean square deviation of 6 measurements, as the 6 values were not consistent within counting errors. The Os measurement was on a nitric-acid-insoluble residue which had been fired to 800°C.





XBL 809-1964

Fig. 1

Table 1. On the possible chondritic nature of the Danish C-T boundary.<sup>d</sup>

	Ganapathy <sup>a</sup> (Average of 2)	Our Work	CI Chondrites
Pt/Ir	0.40	$2.24 \pm 0.23^b$	$1.98^c$
Ni/1000 Ir	6.2	$16.6 \pm 0.5^b$	$20^c$
Co/1000 Ir	0.82	$2.07 \pm 0.03^b$	$1.01^{e,c}$
Au/Ir	0.21	$0.319 \pm 0.020^b$	$0.296^c$

<sup>a</sup>Ratios were calculated from abundances given in Ganapathy.(19)

<sup>b</sup>Pt and Au data are from unpublished work of F. Asaro, H. V. Michel, W. Alvarez and L. W. Alvarez, 1980. The others were published in reference 1.

<sup>c</sup>Au and Ir data are from U. Krähenbühl, J. W. Morgan, R. Ganapathy and E. Anders, *Geochim. Cosmochim. Acta* 37, 1353 (1973).(21) Pt datum is from W. D. Ehmann and D. E. Gillum, *Chem. Geol.* 9, 1 (1972).(27)

<sup>d</sup>If the C-T boundary includes an asteroid component with chondritic abundances, the ratios of the abundances of various elements to Ir should be larger than chondritic because of terrestrial contributions.

<sup>e</sup>The Co abundance is a weighted average (507 ppm) of the data given by Carleton B. Moore in *Handbook of Elemental Abundances in Meteorites* edited by Brian Mason and published by Gordon and Breach Science Publishers (new York), 1971.(23)

the data of Ganapathy is also included in Fig. 1 and Table I. Besides additional measurements of Pt group elements on the Danish and other C-T boundary layers, such measurements are needed on nearby Cretaceous and Tertiary rock formations.  $^{187}\text{Os}/^{186}\text{Os}$  isotopic ratios<sup>(20)</sup> might establish if the Os and Re have maintained chondritic relative abundances throughout the predominant part of their existence since coalescence from dispersed materials billions of years ago.

More studies of the clay mineralogy of the C-T boundary layer are needed. These may indicate if the boundary deposition was associated with an extraordinary event.

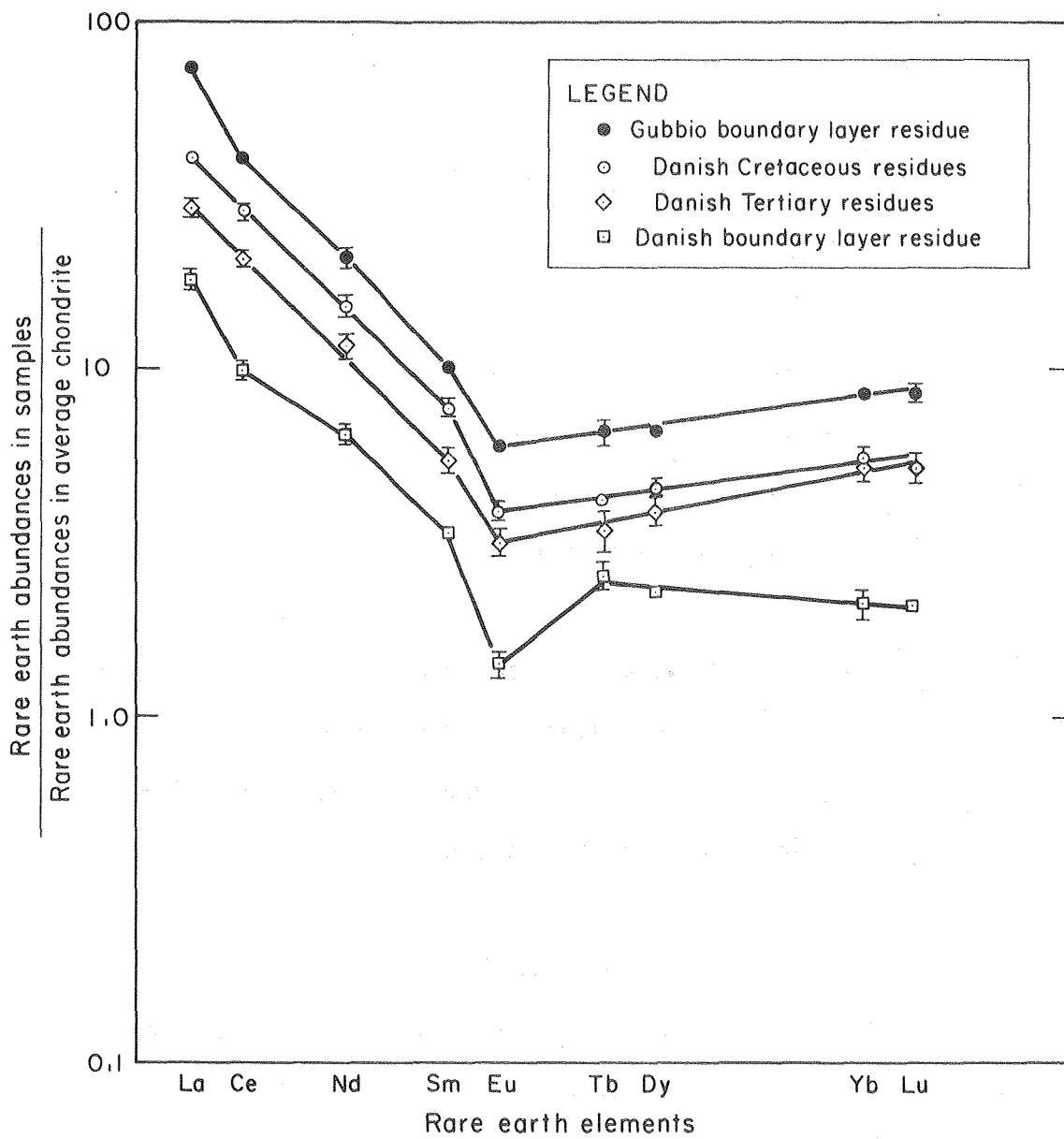
Rare earth abundance patterns, particularly of the clay fraction, may also help determine the origin of the terrestrial components. Rare earth patterns in clay fractions of sediments tend to inherit the patterns of the rocks from which they originated.<sup>(24)</sup> In Figure 2 are shown several examples of the rare earth abundance patterns of nitric-acid-insoluble residues from the Danish boundary layer and the limestones above and below. Such patterns along with the other chemical data may indicate the type of rock from which the boundary layer originated. This may help indicate if the origin was continental, sea floor, rift or otherwise.

The intensity of the C-T iridium anomaly as a function of geographical location along with the mineralogical and chemical studies of the boundary layers may suggest an impact location when considerably more data are obtained.

If the asteroid-impact theory is correct, the extinctions should be repetitive and the Ir anomaly should be observed in other geological

## Figure 2.

Rare earth abundance patterns as normalized to the data of Masuda et al. (except for Tb) for the Leedy L6 meteorite.<sup>(30)</sup> The Tb abundance in meteorites is assumed to be 0.059 ppm. Errors for the Danish Cretaceous (3 samples) and Tertiary (2 samples) nitric-acid-insoluble residues are root-mean-square deviations. Errors for the nitric-acid-insoluble residues from the Gubbio and Danish boundary layers are 1 sigma values of the counting errors.



XBL 7911-13249

Fig. 2

stratigraphic levels corresponding to known extinctions. About five other massive extinctions (besides the one at the end of the Cretaceous Period) have been noted.<sup>(25)</sup> These come at the end of the Cambrian (~500 MY ago), the Ordovician (~435 MY ago), the Devonian (~345 MY ago), the Permian (~230 MY ago) and the Triassic (~195 MY ago) Periods.

In the next four years we hope to have tested the concept of world-wide distribution of the Ir anomaly, tested the premise of an extraordinary extraterrestrial origin of the anomaly, attempted to determine the location of the C-T impact site and tested the repetitive nature of the proposed impact. From the answers to these tests and the questions which will develop, the extent to which the theory is correct can be evaluated and the need and direction for future work can be assessed.

This work was done with support from the Department of Energy under Contract W-7405-ENG-48. Partial support was received from the California Space Group and the National Aeronautics and Space Administration Ames Research Center in the later stages of the work.

#### REFERENCES

1. L. W. Alvarez, W. Alvarez, H. V. Michel and F. Asaro, "Extraterrestrial Cause for the Cretaceous-Tertiary Extinction," *Science* 208, 1095-1108 (1980).
2. W. Alvarez, L. W. Alvarez, F. Asaro and H. V. Michel, "Experimental Evidence in Support of an Extraterrestrial Trigger for the Cretaceous-Tertiary Extinctions," *EOS Trans. Am. Geophys. Union* 60, 734 (1979).

3. W. Alvarez, L. W. Alvarez, F. Asaro and H. V. Michel, "Anomalous iridium levels at the Cretaceous-Tertiary boundary at Gubbio, Italy: Negative results of tests for a supernova origin," Geol. Soc. America Abstract, 11, 378 (1979).
4. D. Russell, L. W. Alvarez, W. Alvarez, H. V. Michel and F. Asaro, unpublished data (1980) cited in Ref. 1.
5. J. Smit and J. Hertogen, "An extraterrestrial event at the Cretaceous Tertiary boundary," Nature 285, 198-200 (1980).
6. M. Arthur, L. W. Alvarez, W. Alvarez, H. V. Michel and F. Asaro, unpublished data, 1980.
7. L. W. Alvarez, W. Alvarez, H. V. Michel and F. Asaro, unpublished data, 1979. Ir values are plotted in Ref. 5.
8. F. C. Wezel, "The Scaglia Rossa Formation of Central Italy: results and problems emerging from a regional study," Ateneo Parmense, Acta Nat. 15, 243-259 (1979).
9. Finn Surlyk, "The Cretaceous-Tertiary boundary event," Nature Vol. 285, 187-188 (1980).
10. Private communication to Walter Alvarez from K. S. Hsü and News Release NSF PR 80-56 (1980).
11. E. S. Öpik, "On the catastrophic effects of collisions with celestial bodies," Irish Astronomical Journal 5, No. 1, 34, 1978.
12. H. C. Urey, "Cometary Collisions and Geological Periods," Nature 242, 32, 1973.
13. K-TEC group (P. Beland et al.). "Cretaceous-Tertiary extinctions and Possible Terrestrial and Extraterrestrial Causes" (Proceedings of Workshop, National Museum of Natural Sciences, Ottawa, 16 and 17 November 1976), pp. 144-149.

14. K. J. Hsü, "Terrestrial catastrophe caused by cometary impact at the end of the Cretaceous," *Nature* 285, 201-203 (1980).
15. Cesare Emiliani, "Death and Renovation at the End of the Mesozoic" *EOS* 61, No. 26, 505-506 (1980).
16. Data for basic materials was taken from "Platinum Metals in Magmatic Sulfide Ores" by A. J. Naldrett and J. M. Duke, *Science* 208, 1417-1424, (1980).
17. L. P. Greenland, D. Gottfried, and R. I. Tilling, "Iridium in some calcic and calc-alkaline batholithic rocks of the western United States," *Chem. Geol.* 14, 117-122 (1974) reported in Ref. 18.
18. J. H. Crocket, "Platinum-Group Elements in Mafic and Ultramafic Rocks: A Survey," *Canadian Mineralogist* 17, 391-402 (1979).
19. R. Ganapathy, "A Major Meteorite Impact on the Earth 65 Million Years Ago. Evidence from the Cretaceous-Tertiary Boundary Clay," *Science* 209, 921-923 (1980).
20. C. J. Allègre and J. M. Luck, "Osmium isotopes as petrogenetic and geological tracers," *Earth Planet. Sci. Lett.* 48, 148-154 (1980).
21. U. Krähenbühl, S. W. Morgan, R. Ganapathy and E. Anders, "Abundance of 17 trace elements in carbonaceous chondrites," *Geochem. Cosmochim. Acta* 37, 1353-1370 (1973).
22. W. D. Ehmann and D. E. Gillum, "Platinum and gold in chondritic meteorites," *Chem. Geol.* 9, 1-11 (1972).
23. Handbook of Elemental Abundances in Meteorites, Brian Mason (ed.), Gordon and Breach Science Publishers, London, 1971.
24. R. L. Cullers, Long-Tsu Yeh, S. Chaudhuri and C. V. Guidotti, "Rare earth elements in Silurian pelitic schists from N. W. Maine," *Geochim. Cosmochim. Acta* 38, 389-400, (1974).



25. N. D. Newell, "Crises in the History of Life," *Scientific American* 208, No. 2, 76-92 (1963).
26. I. Perlman and F. Asaro, "Pottery Analysis by Neutron Activation," in *Science and Archaeology*, R. H. Brill (ed.), MIT press, Cambridge Mass., *Archaeometry* 11, 21-52 (1969).
27. J. Yellin, I. Perlman, F. Asaro, H. V. Michel and D. F. Mosier, "Comparison of Neutron Activation Analysis from the Lawrence Laboratory and the Hebrew University," *Archaeometry* 20, 95-100 (1978).
28. F. Asaro, "Applied Gamma-Ray Spectrometry and Neutron Activation Analysis," *Proceedings of the XX. Colloquium Spectroscopicum Internationale and 7. International Conference on Atomic Spectroscopy Praha 1977 Invited Lectures II*, 413-426.
29. W. M. Napier and S. V. M. Clube, "A theory of terrestrial catastrophism," *Nature (London)* 282, 455-459 (1979).
30. A. Masuda, N. Nakamura and T. Tanaka, "Fine structures of mutually normalized rare-earth patterns of chondrites," *Geochim. Cosmochim. Acta* 37, 239-248 (1973).

